A chalcogen-bonded complex $\text{H}_3\text{N}\cdots\text{S=\hspace{1pt}C=S}$ formed by ammonia and carbon disulfide characterised by chirped-pulse, broadband microwave spectroscopy
A chalcogen-bonded complex $\text{H}_3\text{N} \cdots \text{S} = \text{C} = \text{S}$ formed by ammonia and carbon disulfide characterised by chirped-pulse, broadband microwave spectroscopy

I. INTRODUCTION

A wide range of non-covalent, pairwise interactions of molecules in the gas phase has been investigated spectroscopically in the last 50 years. The most important of these is the hydrogen bond because of its ubiquity in Chemistry and Biology. The halogen bond has become of increasing interest since the 1990s, and its properties have been shown[3,4] to parallel those of the hydrogen bond in many respects. Modern definitions[5,6] of both these important interactions have been published recently. Tetrrel, pnictogen, chalcogen, and coinage-metal bonds are less well known non-covalent interactions and were given names only during the last seven years,[5–8] even though they had been characterised extensively in the gas phase during the last 50 years.[9] These newer types of pairwise interaction can be written in general as $\text{B} \cdots \text{E} = \text{R}$, where $\text{E}$ is an atom of group 14, 15, 16, or 11, respectively, $\text{R}$ is the remainder of the molecule $\text{E} = \text{R}$, and $\text{B}$ is a Lewis base. The atom $\text{E}$ is the...
most electrophilic region of E–R and interacts with a nucleophilic region of B, usually a non-bonding (n) electron pair or a π-bonding electron pair. As an example, the C atom is the most electrophilic region of CO\textsubscript{2} and interacts with the n-pair of NH\textsubscript{3} to form a T-shaped complex in which the linear CO\textsubscript{2} molecule acts as the bridge of T while the C\textsubscript{3} symmetry axis of NH\textsubscript{3} forms the stem.\textsuperscript{10} Thus, the weak intermolecular bond is a tetrel bond.

Carbon disulphide (CS\textsubscript{2}) is an isostuctural congener of CO\textsubscript{2} and therefore might be expected also to form tetrel bonds in which its C atom again acts as the electrophilic region when interacting with Lewis bases such as NH\textsubscript{3}. Examination of the molecular electrostatic surface potentials (MESPs) of CO\textsubscript{2} and CS\textsubscript{2} calculated at the MP2/6-311++G\textsuperscript{*} level with Spartan\textsuperscript{11} and shown in Fig. 1 reveals that the electrophilic (blue, most positive potential) region is differently placed in these two molecules, however. CO\textsubscript{2} has an electrophilic (blue) band around the C atom, while CS\textsubscript{2} has no such band, but instead its most electrophilic region lies near each S atom along the C\textsubscript{∞} axis. This indicates that CS\textsubscript{2} and NH\textsubscript{3} are likely to form a complex H\textsubscript{3}N⋅⋅⋅S=C=S of C\textsubscript{3v} symmetry. To the best of our knowledge, the only complex of CS\textsubscript{2} investigated by means of its rotational spectrum is that with H\textsubscript{2}O, for which Ogata and Low\textsuperscript{12} report that the most probable geometry is H\textsubscript{2}O⋅⋅⋅S=C=S, planar with C\textsubscript{2v} symmetry.

We report here a detailed investigation, by chirped-pulse broadband microwave spectroscopy, of the ground-state rotational spectra of fourteen isotopologues of a complex formed by ammonia with carbon disulphide. Interpretation of the spectroscopic constants thereby determined in the light of a simple model of the complex, allows the symmetry, the order of the atoms, the geometry, the strength of binding (as measured by the intermolecular stretching force constant k\textsubscript{S}), and information about the subunit dynamics to be derived. The results can then be compared with those from good quality \textit{ab initio} calculations, as recently published.\textsuperscript{15}

II. EXPERIMENTAL

The chirped-pulse, Fourier-transform microwave (CP-FTMW) spectrometer used at Newcastle University has been described in detail elsewhere.\textsuperscript{16} The spectrometer can be configured to operate in either the 2.0–8.0 or 7.0–18.5 GHz frequency bands during individual experiments. Spectra were recorded across each of these bands during the present work.

The generation of CS\textsubscript{2}⋅⋅⋅NH\textsubscript{3} was achieved by mixing CS\textsubscript{2} and NH\textsubscript{3} within an argon buffer gas and pulsing this sample through a supersonic valve (Parker, General Series 9) into a vacuum chamber at a backing pressure of 7 bars. Each of CS\textsubscript{2} and NH\textsubscript{3} were present in the gas sample at low concentrations of 1% and 2%, respectively. Isotopically enriched samples of \textsuperscript{13}C\textsubscript{34}N\textsubscript{3} or ND\textsubscript{3} were used to permit experiments on isotopologues containing \textsuperscript{15}N or D, respectively. Coherent polarisation of the molecular ensemble is induced by a microwave pulse (of duration 1 \(\mu\)s) that sweeps from high to low frequency. Propagation of this microwave pulse is perpendicular to the direction of travel of molecules introduced from the valve. The subsequent relaxation of the molecular ensemble was recorded and digitised by a 100 GSample/s oscilloscope (Tektronix DPO72304SX) in the form of a free induction decay (FID) of duration 20 \(\mu\)s.

The sequence of polarisation pulse followed by free induction decay is complete within less than 25 \(\mu\)s. Molecules in the expanding jet are spatially positioned to interact with the microwave pulse for longer than 200 \(\mu\)s. The time scale thus allows for eight iterations of the spectral acquisition per valve pulse. An arbitrary waveform generator, phase-locked dielectric resonant oscillator, and oscilloscope are locked to a Rb-clock, which provides a 10 MHz reference that allows coherent averaging of the data in the time domain. The FIDs are co-added in the time domain prior to fast Fourier transformation (FFT) using a Kaiser-Bessel window function to generate the frequency domain spectrum. The resulting spectra have linewidths of 100 kHz (FWHM), consistent with standard deviations of approximately 10 kHz achieved when fitting transitions to the predictions of a model Hamiltonian.

III. RESULTS

A. Observed rotational spectra

The rotational spectra of the isotopologues H\textsubscript{3}N⋅⋅⋅S
\[=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{34}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{33}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{32}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{31}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{30}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{29}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{28}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{27}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{26}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{25}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{24}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{23}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{22}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{21}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{20}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{19}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{18}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{17}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{16}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{15}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{14}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{13}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{12}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{11}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{10}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{9}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{8}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{7}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{6}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{5}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{4}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{3}\text{N}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{2}\text{S}=C=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{1}\text{C}=S, \text{H}_3\text{N} \cdot \cdot \cdot ^{0}\text{N}=C=S \]
H$_{15}N\cdots S^{13}C=S$, H$_{15}N\cdots S^{33}S=C=S$, and H$_{15}N\cdots S=C=^{33}S$ (absence of a superscript mass number implies the most abundant nuclide) were observed, either in their natural abundance by using an isotopically normal mixture of ammonia and carbon disulphide or a mixture containing an isotopically enriched sample of $^{15}$NH$_3$. Each spectrum consisted of rotational transitions of the type $J + 1 \leftarrow J$, $K \leftarrow K$ expected for the vibrational ground-state of a prolate symmetric-top molecule. Only transitions having $K = 0$ and $K = 1$ had a detectable intensity presumably because $K = 2$ states lose their room temperature population by transfer to $K = 1$ states during the supersonic expansion of the gas mixture, while transfer of population from $K = 1$ to $K = 0$ states by collision is spin-forbidden. In the $^{14}$N-containing species, each $J + 1 \leftarrow J$, $K \leftarrow K$ transition exhibited a hyperfine pattern characteristic of coupling of the $^{14}$N nuclear spin vector $I_N$ to the framework angular momentum vector $J$ via the interaction of the $^{14}$N nuclear electric quadrupole moment with the electric field gradient $(efg)$ at that nucleus. Figure 2 shows a recording of the $^{14}$N nuclear electric quadrupole moment with the electric field gradient vector $Q_X$ at the framework nucleus X (in $^{14}$N or $^{33}$S) and $\nabla E_X$ is the electric field gradient dyadic at nucleus X. Since the electric quadrupole moment dyadic of nucleus X ($= ^{14}$N or $^{33}$S) and $\nabla E_X$ is the conventional electric quadrupole moment of nucleus X, and $e$ is the proton charge. The spectroscopic constants determined in the final cycle of the least-squares fit for each of the 10 symmetric-top isotopologues are shown in Table I. Spectroscopic constants determined for the four asymmetric-rotor isotopologues $^{14}$NH$_2$D$^{32}$S$=^{12}$C$=^{32}$S, $^{14}$NH$^{34}$N$=^{32}$S$=^{12}$C$=^{32}$S, $^{14}$NH$^{32}$N$=^{32}$S$=^{12}$C$=^{32}$S, and $^{14}$ND$^{34}$N$=^{32}$S$=^{12}$C$=^{32}$S are also shown in Table I. Each transition, only $K_1 = 0$ transitions could be observed, a familiar consequence of the breaking of $C_2v$ symmetry and thereby relaxation of the $K + 1 \leftarrow K = 1 \rightarrow 0$ spin-forbidden collisional propensity rule mentioned earlier. Because the $K_1 = 1$ levels are several cm$^{-1}$ higher in wavenumber than the $K_1 = 0$ levels in the D species, they are susceptible to cooling in the expansion. The $^{14}$N nuclear quadrupole hyperfine structure was insufficiently resolved for these species, and each spectrum was fitted by using the appropriate asymmetric-rotor Hamiltonian to give the only determinable spectroscopic constants ($B + C/2$ and $\Delta_1$, as included in Table I). Observed frequencies and the spectroscopic constants determined in the final cycle of the PGOPHER fit for all isotopologues investigated are available in the supplementary material.

**B. Experimentally determined distance $r(N\cdots S)$**

The magnitude of the changes in the rotational constants $B_0$ of the parent species on isotopic substitution at each atom establishes that the order of the atoms is H$_{15}N\cdots S^{32}$C$=^{32}$S. The nature of the rotational spectra observed shows that the complex is a symmetric-top molecule. The fact that the interaction between the two molecules is very weak (see Sec. III D) suggests that we assume the $r_0$ geometries of ammonia and carbon disulphide are unchanged on complex formation when determining a $r_0$ value of the distance $r(N\cdots S)$ in the complex. The $r_0$ geometry of NH$_3$ was determined by fitting the ground-state rotational constants$^{16}$ $B_0$ and $C_0$ of $^{14}$NH$_3$ and $^{13}$NH$_3$ isotopologues, while that of CS$_2$ was similarly obtained from a fit of the ground-state rotational constants of several isotopologues measured in a recent high-resolution examination of several isotopologues measured in the Raman spectrum.$^{17}$ In each case, Kisiel’s program STRFIT$^{18}$ was employed and the results are in Table II. The observed $^{14}$N nuclear quadrupole

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**Fig. 2.** The $J + 1 \leftarrow J = 1 \rightarrow 0$ transition of the parent isotopologue of H$_2N\cdots S=C=S$ showing the three $^{14}$N nuclear quadrupole hyperfine components. This was recorded by collecting $1.15 \times 10^6$ free induction decays. The red spectrum is that simulated with PGOPHER by using the spectroscopic constants given in Table I.
The zero-point motion of the complex $H_3N\cdots S=C=S$.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>$B_0$ (MHz)</th>
<th>$D_1$ (kHz)</th>
<th>$D_{JK}$ (MHz)</th>
<th>$\chi^{(4)}$ (N) (MHz)</th>
<th>$\chi^{(3)}$ (S) (MHz)</th>
<th>N^a</th>
<th>$\sigma_{rms,b}$ (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_3N\cdots S=C=S$</td>
<td>1018.968 00(25)^b</td>
<td>0.6688(25)</td>
<td>0.295 76(20)</td>
<td>$-2.8459(37)$</td>
<td>\ldots</td>
<td>55</td>
<td>7.5</td>
</tr>
<tr>
<td>$H_3N\cdots ^{34}S=C=S$</td>
<td>1017.259 12(24)</td>
<td>0.6603(20)</td>
<td>0.294 77(21)</td>
<td>$-2.8487(55)$</td>
<td>\ldots</td>
<td>29</td>
<td>5.5</td>
</tr>
<tr>
<td>$H_3N\cdots S=^{13}C=S$</td>
<td>1017.342 86(49)</td>
<td>0.6683(37)</td>
<td>0.294 75(38)</td>
<td>$-2.801(27)$</td>
<td>\ldots</td>
<td>18</td>
<td>8.6</td>
</tr>
<tr>
<td>$H_3N\cdots S=C=^{14}S$</td>
<td>995.274 80(35)</td>
<td>0.6319(28)</td>
<td>0.283 26(30)</td>
<td>$-2.8493(88)$</td>
<td>\ldots</td>
<td>27</td>
<td>7.6</td>
</tr>
<tr>
<td>$H_3N\cdots S=S=^{33}S$</td>
<td>988.089 09(33)</td>
<td>0.6390(27)</td>
<td>0.275 51(25)</td>
<td>\ldots</td>
<td>\ldots</td>
<td>17</td>
<td>5.8</td>
</tr>
<tr>
<td>$H_3N\cdots ^{34}S=S=^{33}S$</td>
<td>986.680 68(39)</td>
<td>0.6331(36)</td>
<td>0.274 82(32)</td>
<td>\ldots</td>
<td>\ldots</td>
<td>16</td>
<td>6.8</td>
</tr>
<tr>
<td>$H_3N\cdots S=^{33}S$</td>
<td>986.408 21(55)</td>
<td>0.6556(44)</td>
<td>0.268 27(31)</td>
<td>\ldots</td>
<td>\ldots</td>
<td>8</td>
<td>4.7</td>
</tr>
<tr>
<td>$H_3N\cdots S=S=^{34}S$</td>
<td>965.040 52(57)</td>
<td>0.6082(54)</td>
<td>0.265 41(25)</td>
<td>\ldots</td>
<td>\ldots</td>
<td>14</td>
<td>7.9</td>
</tr>
<tr>
<td>$H_3N\cdots ^{33}S=S=^{34}S$</td>
<td>987.377 38(68)</td>
<td>[0.633(36)]^b</td>
<td>0.276 94(50)</td>
<td>\ldots</td>
<td>$-16.135(76)$</td>
<td>18</td>
<td>14.2</td>
</tr>
<tr>
<td>$H_3N\cdots S=S=^{33}S$</td>
<td>976.289 88(68)</td>
<td>[0.6082(54)]^b</td>
<td>0.266 37(37)</td>
<td>\ldots</td>
<td>$-16.495(29)$</td>
<td>22</td>
<td>14.1</td>
</tr>
<tr>
<td>$H_2DN\cdots S=C=S$</td>
<td>981.558 9(12)^b</td>
<td>0.646(10)</td>
<td>\ldots</td>
<td>\ldots</td>
<td>\ldots</td>
<td>6</td>
<td>14.1</td>
</tr>
<tr>
<td>$HD_2N\cdots S=C=S$</td>
<td>947.493 8(13)</td>
<td>0.613(11)</td>
<td>\ldots</td>
<td>\ldots</td>
<td>\ldots</td>
<td>6</td>
<td>14.9</td>
</tr>
<tr>
<td>$H_2DN\cdots S=S=^{33}S$</td>
<td>980.806 8(19)</td>
<td>0.611(16)</td>
<td>\ldots</td>
<td>\ldots</td>
<td>\ldots</td>
<td>5</td>
<td>19.1</td>
</tr>
<tr>
<td>$H_2DN\cdots S=S=^{34}S$</td>
<td>958.735 5(12)</td>
<td>0.604(10)</td>
<td>\ldots</td>
<td>\ldots</td>
<td>\ldots</td>
<td>6</td>
<td>14.4</td>
</tr>
</tbody>
</table>

^a Number of frequencies in the fit.  
^b Root mean square deviation of the fit.  
^c Numbers in parentheses are one standard deviation in units of the last significant figure.  
^d Value for $D_1$ fixed at that for $H_3^{15}N\cdots S=C=S$ and $H_3^{13}N\cdots S=C=^{34}S$ isotopologue, respectively. Only three $J$ available for $H_3^{15}N\cdots S=C=S$ and $H_3^{13}N\cdots S=C=^{34}S$, and three $J$ dependent terms cannot be well defined.  
^e $(B + C)/2$ for asymmetric-top isotopologues containing D.

The effects of the intermolecular bending modes, when determining the distance $r(N\cdots S)$ from ground-state moments of inertia. The model of the complex shown schematically in Fig. 3 allows for the contribution of these modes but not the intermolecular stretching mode. Each subunit $NH_3$ and S=C=S is assumed to execute the indicated angular oscillations, assumed axially symmetric (two-dimensionally isotropic), with respect to its centre of mass, but with the distance $r_{cm}$ between the mass centres fixed (i.e., no intermolecular stretching). In Fig. 3, $\theta$ is the angle between the line $r_{cm}$ and the $C_3$ axis of $NH_3$ and $\phi$ is the corresponding angle made with the $C_3$ axis of CS$_2$. By using this model, it can be shown that $I_b^{NH_3}$ of the complex is related to the ground-state principal moments of inertia $I_b^{NH_3}$, $I_c^{NH_3}$, and $I_b^{CS_2}$ of the components (as calculated from their observed rotational constants recorded in Table II) by

### Table II. Some molecular properties of ammonia and carbon disulphide.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$B_0$ (MHz)</th>
<th>$C_0$ (MHz)</th>
<th>$r_0$ geometry</th>
<th>$\chi^{(4)}$(N) (MHz)</th>
<th>$\chi^{(3)}$(S) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{14}NH_3$</td>
<td>298 115.37^a</td>
<td>187 405^b</td>
<td>$r_0(N-H) = 1.015 57 , Å$</td>
<td>$\chi^{(4)}(N-H) = 107.277^c$</td>
<td>$-4.08983(2)^d$</td>
</tr>
<tr>
<td>$^{15}NH_3$</td>
<td>297 388.12^a</td>
<td>187 405^b</td>
<td>\ldots</td>
<td>\ldots</td>
<td>\ldots</td>
</tr>
<tr>
<td>$^{32}S=^{12}C=^{32}S$</td>
<td>3271.5170(7)^a</td>
<td>3271.5170(7)^a</td>
<td>$r_0(C=S) = 1.554 27(1)^f , Å$</td>
<td>\ldots</td>
<td>$-17.1(6)^{f}$</td>
</tr>
</tbody>
</table>

^a Reference 16.  
^b Calculated from the $r_0$ geometry.  
^c Calculated by fitting $B_0$ values of $^{14}NH_3$ and $^{15}NH_3$.  
^d Reference 19.  
^e Reference 17.  
^f Calculated by fitting $B_0$ values of six isotopologues of S=C=S given in Ref. 17.  
^g Calculated ab initio (see Sec. III C for details).
TABLE III. Some properties of the complex $\text{H}_3\text{N} \cdots \text{S}=\text{C}=\text{S}$ derived from the rotational spectra of ten symmetric-top isotopologues.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>$r_{cm}$ (Å)</th>
<th>$r(N \cdots S)$ (Å)</th>
<th>$k_{av}$ (N m$^{-1}$)</th>
<th>$10^{12} k_{dd}$ (J$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{S}$</td>
<td>4.959(10)</td>
<td>3.338(10)</td>
<td>3.95(2)</td>
<td>4.600(3)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{C}=\text{S}$</td>
<td>4.999(10)</td>
<td>3.338(10)</td>
<td>3.91(2)</td>
<td>4.583(3)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{S}=\text{S}$</td>
<td>4.959(10)</td>
<td>3.338(10)</td>
<td>3.95(2)</td>
<td>4.600(6)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{C}=\text{C}=\text{S}$</td>
<td>4.920(10)</td>
<td>3.338(10)</td>
<td>3.95(1)</td>
<td>4.600(14)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{C}=\text{S}$</td>
<td>4.954(10)</td>
<td>3.337(10)</td>
<td>4.04(2)</td>
<td>4.643(5)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{C}=\text{C}=\text{C}=\text{S}$</td>
<td>4.994(10)</td>
<td>3.337(10)</td>
<td>3.93(3)</td>
<td>4.599(4)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{S}=\text{S}$</td>
<td>4.954(10)</td>
<td>3.337(10)</td>
<td>3.89(3)</td>
<td>4.755(5)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{C}=\text{C}=\text{C}=\text{C}=\text{S}$</td>
<td>4.915(10)</td>
<td>3.338(10)</td>
<td>4.00(2)</td>
<td>4.642(7)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{C}=\text{S}=\text{S}$</td>
<td>4.934(10)</td>
<td>3.338(10)</td>
<td>4.01(2)</td>
<td>4.636(8)</td>
</tr>
<tr>
<td>$\text{H}_3\text{N} \cdots \text{S}=\text{C}=\text{C}=\text{S}=\text{S}$</td>
<td>4.974(10)</td>
<td>3.337(10)</td>
<td>...</td>
<td>4.689(18)</td>
</tr>
</tbody>
</table>

*Calculated by using Eq. (2).
*Calculated by using Eq. (5).
*Calculated by using Eq. (6).
The coupling constant of the isotopologues \( \text{H}_3\text{S}^{15} \) = two (inner and outer) \( \text{S} \) coupling constants for the free molecule \( \text{S} = \text{C} = \text{S} \) in column 5. We note that the difference between columns 5 and 6 is negligible in the present context, that is, the mean of the inner and outer \( \text{S} \) coupling constants of \( \text{H}_3\text{N}\cdots \text{S} = \text{C} = \text{S} \) is essentially identical to the \( \text{S} \) coupling constant of the free \( \text{CS}_2 \) molecule. Since the calculations refer to the \( \text{C}_3 \) equilibrium geometry of \( \text{H}_3\text{N}\cdots \text{S} = \text{C} = \text{S} \), in which there is no zero-point oscillation of the subunits (\( \theta = \phi = 0 \)), this analysis suggests that the mean of the values of the \( \chi_{\text{obs}}(\text{S}) \) for \( \text{H}_3\text{N}\cdots \text{S} = \text{C} = \text{S} \) and \( \text{H}_3\text{S}\cdots \text{S} = \text{C} = \text{S} \) should be used as \( \chi_{\text{av}}(\text{S}) \) (i.e., corrected for the efg due to \( \text{NH}_3 \)) when deriving \( \phi \) from Eq. (4). Thus, \( \chi_{\text{av}}(\text{S}) = (-16.14 - 16.50)/2 = -16.32 \text{MHz} \). When \( \chi_{\text{av}}(\text{S}) = -16.32 \text{MHz} \) and \( \chi_{\text{av}}(\text{S}) = -17.16 \text{MHz} \) are used in Eq. (4), the result is \( \phi = \cos^{-1}(\cos^2\phi)^{1/2} = 10(3)^\circ \).

A comparison of \( \chi_{\text{av}}(\text{N}) \) for the free ammonia molecule with that of \( \text{H}_3\text{N}\cdots \text{S} = \text{C} = \text{S} \) when both are calculated at the \( \text{B3LYP}/\text{aug-cc-pVZ} \) level of theory shows a constant difference of only \( -0.04 \text{MHz} \) for \( \text{N} \) in the range of 3–6. For

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**Table IV.** Calculated values of the \( ^{33}\text{S} \) nuclear quadrupole coupling constant of \( \text{CS}_2 \), \( \text{CS} \), and \( \text{OCS} \) at the \( \text{B3LYP} /\text{aug-cc-pV} /n+6\text{Z} \) level of theory for \( n = 3, 4, 5, \) and 6 and its estimated value for the zero-point state of \( \text{CS}_2 \).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Basis function</th>
<th>( \chi_{\text{calc}}(\text{S}) ) (MHz)</th>
<th>( \chi_{\text{obs}}(\text{S}) ) (MHz)</th>
<th>( \chi_{\text{obs}}(\text{S}) )/( \chi_{\text{calc}}(\text{S}) )</th>
<th>Est. value ( \chi_{\text{corr}}(\text{S}) ) (MHz) for ( \text{CS}_2 )</th>
<th>Est. value ( \chi_{\text{corr}}(\text{S}) ) (MHz) for ( \text{CS}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CS}_2 )</td>
<td>( n = 6 )</td>
<td>–16.845</td>
<td>…</td>
<td>…</td>
<td>–17.750</td>
<td>–16.520</td>
</tr>
<tr>
<td></td>
<td>( n = 5 )</td>
<td>–16.958</td>
<td>…</td>
<td>…</td>
<td>–17.819</td>
<td>–16.534</td>
</tr>
<tr>
<td></td>
<td>( n = 3 )</td>
<td>–14.966</td>
<td>…</td>
<td>…</td>
<td>–15.442</td>
<td>–16.162</td>
</tr>
<tr>
<td>( \text{CS} )</td>
<td>( n = 6 )</td>
<td>+12.172</td>
<td>+12.8256(2)</td>
<td>1.0537</td>
<td>1.0508</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( n = 5 )</td>
<td>+12.206</td>
<td>…</td>
<td>1.0508</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( n = 4 )</td>
<td>+11.629</td>
<td>…</td>
<td>1.029</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( n = 3 )</td>
<td>+12.430</td>
<td>…</td>
<td>1.0318</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{OCS} )</td>
<td>( n = 6 )</td>
<td>–29.692</td>
<td>–29.118(1)</td>
<td>0.9807</td>
<td>0.9750</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( n = 5 )</td>
<td>–29.865</td>
<td>…</td>
<td>0.9750</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( n = 4 )</td>
<td>–26.679</td>
<td>…</td>
<td>1.0914</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( n = 3 )</td>
<td>–26.964</td>
<td>…</td>
<td>1.0799</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^{a} \text{Reference 26} \)

\( ^{b} \text{Reference 27} \)

---

**Table V.** \( ^{33}\text{S} \) nuclear quadrupole coupling constants of \( \text{H}_3\text{N}\cdots \text{S} = \text{C} = \text{S} \) and \( \text{S} = \text{C} = \text{S} \) calculated at the \( \text{B3LYP} /\text{aug-cc-pV} /n+6\text{Z} \) level of theory.

<table>
<thead>
<tr>
<th>Basis</th>
<th>( \chi(\text{S}) ) (MHz)</th>
<th>( \chi(\text{S}) ) (MHz)</th>
<th>( \chi(\text{S}) ) (MHz)</th>
<th>( \chi(\text{S}) ) (MHz)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 4 )</td>
<td>–14.198</td>
<td>–15.539</td>
<td>–14.869</td>
<td>–14.934</td>
<td>0.065</td>
</tr>
<tr>
<td>( n = 5 )</td>
<td>–16.230</td>
<td>–17.646</td>
<td>–16.938</td>
<td>–16.958</td>
<td>0.020</td>
</tr>
<tr>
<td>( n = 6 )</td>
<td>–16.055</td>
<td>–17.494</td>
<td>–16.775</td>
<td>–16.845</td>
<td>0.070</td>
</tr>
</tbody>
</table>

\( ^{a} \text{Subscript } i = \text{inner}. \)

\( ^{b} \text{Subscript } o = \text{outer}. \)

\( ^{c} \text{Subscript } av \text{ indicates the average of } i \text{ and } o \text{ values.} \)
example, the two values calculated at the $n = 6$ level are
$-4.438$ MHz for NH$_3$ and $-4.401$ MHz for H$_3$N···S=C=S. Thus, the
free molecule value is $\chi(\text{H}_3\text{N}) = -4.090$ MHz (included
in Table V) can be corrected to $\chi^{\text{corr}}(\text{H}_3\text{N}) = -4.090 - 0.04$ MHz
$\approx -4.13$ MHz, which when used in Eq. (4) with the observed
value $\chi(\text{H}_3\text{N}) = -2.846(4)$ MHz for H$_3$N···SCS gives $\theta_{av}$
$= \cos^{-1}(\cos^2 \theta)^{1/2} = 2^\circ$, with a liberal range of ±3°
assumed from consideration of the related average $\langle \theta^2 \rangle^{1/2}$ determined
in Sec. III D.

D. Intermolecular stretching and bending
force constants

There are two measures of the strength of the interaction
of NH$_3$ and S=C=S to form the complex H$_3$N···S=C=S.
The first is the dissociation energy $D_c$. The second is the
intermolecular stretching force constant $k_D$, which is a measure
of the resistance to an infinitesimal displacement along the weak
bond direction. Millen$^{28}$ showed that $k_D$ is simply related to
the centrifugal distortion constant $D_2$ and the rotational con-
stant $B_0$ for symmetric-top complexes such as H$_3$N···S=C=S
by
$$k_D = \left\{16\pi^2 \mu B_0^2/D_0\right\} \left[1 - (B_0/B_{\text{NH}_3}) - (B_0/B_{\text{CS}_2})\right], \tag{5}$$
where $\mu$ is as defined earlier and B$^{\text{NH}_3}$ and B$^{\text{CS}_2}$ are the rota-
tional constants of the separate components. The derivation
of Eq. (5) assumes rigid subunits and ignores terms beyond
quadratic in the potential energy function. The values of $k_D$ for
the symmetric-top isotopologues calculated using Eq. (5)
with the ground-state spectroscopic constants of the com-
plex (Table I) and the separate components (Table II) are
included in Table III. The mean is 3.95(5) N m$^{-1}$, and is
slightly smaller than that ($k_D = 5.3$ N m$^{-1}$) recently calcu-
lated$^{13}$ at the CCSD(T)/aug-cc-pVTZ level of theory. The
difference arises in part because, strictly, equilibrium rather than
zero-point spectroscopic constants should be used in
Eq. (5).

The intermolecular bending force constant $k_{\text{HHH}}$ can also
be estimated from centrifugal distortion constants. If the model
for the motion of the subunits discussed in Sec. III B and
illustrated in Fig. 3 is assumed and each subunit is again
described as a two-dimensional isotropic harmonic oscillator,
the quadratic force constant $k_{\text{HHH}}$ is related to the centrifugal
distortion constant $D = 2D_2 + D_4$ by$^{29}$
$$k_{\text{HHH}} = (2\hbar/D)B_0^2 \left[B_0/B_{\text{NH}_3} - 1\right]^{1/2}. \tag{6}$$

Equation (6) applies to symmetric-top isotopomers of
H$_3$N···S=C=S only. Values of $k_{\text{HHH}}$ estimated by using
$D = 2D_2 + D_4$ and $B_0$ from Table I and $B_{\text{NH}_3}$ for the free ammonia
molecule (Table II) are included in Table III for the symmet-
topic isotopologues of the complex. The errors transmitted
from those in the centrifugal distortion constants when using
Eq. (6) are small, and presumably differences in $k_{\text{HHH}}$ outside
the quoted errors arise mainly from limitations of the model used
to obtain Eq. (6).

An alternative to the angle $\theta_{av} = \cos^{-1} \langle \cos^2 \theta \rangle^{1/2}$ defined
in Sec. III B is $\langle \theta^2 \rangle^{1/2}$, which can be estimated from $k_{\text{HHH}}$. It
has been shown that $\langle \theta^2 \rangle$ is related to $k_{\text{HHH}}$ using the following expression:$^{30}$
$$\langle \theta^2 \rangle = \left(\hbar/2\pi\right) \left(k_{\text{HHH}}B_{\text{H}_3\text{N}}\right)^{-1/2}, \tag{7}$$
if the motion of the NH$_3$ subunit in the symmetric-top com-
plex can be treated as a two-dimensional isotropic oscillator.
Using the values of $B_{\text{H}_3\text{N}}$ implied by the monomer rotatio-
tional constants given in Table II, we estimate that the mean
value $\langle \theta^2 \rangle^{1/2} = 31.00(1)$° for the ten symmetric-top isotopo-
logues of H$_3$N···S=C=S. If $\langle \theta^2 \rangle^{1/2}$ is not too large, we can
assume that $\langle \theta^2 \rangle^{1/2} = \cos^{-1} \langle \cos^2 \theta \rangle^{1/2}$, which is consistent with
the choice of the range for the angle $\theta_{av} = 27(3)^\circ$ used in
connection with the geometry determination discussed in
Sec. III B.

IV. DISCUSSION

The ground-state rotational spectra of 14 isotopologues
of the complex H$_3$N···S=C=S formed between ammonia and
carbon disulphide in the gas phase have been analyzed to
yield rotational constants, centrifugal distortion constants,
and, where appropriate, $^{14}$N and $^{33}$S nuclear quadrupole
coupling constants. The nature of the spectra and the changes
that accompany the isotopic substitutions establish that the
complex is a symmetric-top molecule of $C_3v$ symmetry with
the atoms in the order H$_3$N···S=C=S. Thus, the intermolec-
ular bond is between the non-bonding electron pair on N and
the electrophilic region near S on the C$_3$ axis of the com-
plex, that is, it is the type of non-covalent interaction now
referred to as a chalcogen bond. A simple model used to
account for the contribution of the angular oscillations to the
zero-point motion leads to the distance $r(\text{N}···\text{S}) = 3.338(10)$ Å,
which is, as expected, longer than the equilibrium value
3.304 Å obtained from a recent ab initio calculation$^{15}$ at the
CCSD(T)/aug-cc-pVTZ level. Interpretations of the centrifu-
gal distortion constants of the complex lead to the intermolec-
ular stretching and bending force constants $k_D = 3.95(5)$ N m$^{-1}$
and $k_{\text{HHH}} = 4.63(5) \times 10^{-21}$ J, which indicate that the inter-
molecular chalcogen bond is weak. For comparison, values of
$k_D = 12.2$ and 12.7 N m$^{-1}$ and $k_{\text{HHH}} = 27.5 \times 10^{-21}$ and 42.2 $\times 10^{-21}$ J
have been reported by these methods$^{30}$ for the hydrogen-
bonded complex H$_3$N···HCN and the halogen–bonded com-
plex H$_3$N···Cl$_2$, respectively. The value of $\langle \theta^2 \rangle^{1/2} = 31^\circ$ deter-
mined from $k_{\text{HHH}}$ has been shown to be consistent with the
angular oscillation $\theta_{av} = \cos^{-1} \langle \cos^2 \theta \rangle^{1/2}$ for the NH$_3$
subunit deduced from the $^{14}$N nuclear quadrupole coupling
constant.

SUPPLEMENTARY MATERIAL

See supplementary material for outputs from the final
cycle of the PGOPHER fits of transitions of each isotopologue
investigated and from the GAUSSIAN calculations.

ACKNOWLEDGMENTS

We thank Newcastle University for a research studentship
(for E.G.), the University of Bristol for a Senior Research

Published under license by AIP Publishing
Fellowship (for A.C.L.), and the Australian Research Council for a Discovery Early Career Research Fellowship (No. DE180101194) (for C.M.). The authors thank the Engineering and Physical Sciences Research Council (UK) and the European Research Council for funding construction of the instrument used for this work (under Grant Nos. EP/G026424/1 and CPFTMW-307000, respectively).

REFERENCES